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APPLICATION FOR LETTERS PATENT

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**Methods of Removing at Least Some Of A
Material from A Semiconductor Substrate**

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1 Methods of Removing at Least Some Of A Material from
2 A Semiconductor Substrate

3 TECHNICAL FIELD

4 The invention pertains to methods of forming and utilizing ozone
5 to remove at least some of a material from a semiconductor substrate.
6 In particular applications, the invention pertains to methods of utilizing
7 organic material vapors in combination with ozone to remove materials
8 from semiconductor substrates.

9
10 BACKGROUND OF THE INVENTION

11 It is common to utilize ozone for removing materials from over
12 semiconductor substrates during semiconductor device fabrication. For
13 instance, ozone can be utilized for removing photoresist and other
14 organic materials. The ozone is typically generated proximate to, or
15 within, a reaction chamber. The semiconductor substrate is provided
16 within the reaction chamber, and the ozone is contacted with the
17 material which is to be removed.

18 Ozone can be utilized for removing organic materials, such as, for
19 example, photoresist, in that the ozone can oxidize the organic material
20 and thereby convert the organic material to a form which is more readily
21 removed from over a semiconductor substrate than was the organic
22 material prior to oxidation.
23

1 A method of forming ozone is to feed a diatomic oxygen (O_2)
2 containing feed gas into an ozone generator. The feed gas is generally
3 about 99.9% O_2 (by volume), with the remaining 0.1% of the feed gas
4 comprising mostly nitrogen (N_2). Occasionally, additional nitrogen may
5 be spiked into the feed gas to raise a concentration of nitrogen up to
6 about 5%. A reason for utilizing the relatively low purity oxygen as a
7 feed gas for generating ozone is that it can be cheaper than higher
8 purity oxygen. Another reason is that there can be a reduced risk of
9 flame or explosion in utilizing a lower purity oxygen, relative to that
10 which would exist in utilizing a higher purity oxygen.

11 The invention encompasses new methods of forming and utilizing
12 ozone in removing materials from over semiconductor substrates.

14 SUMMARY OF THE INVENTION

15 The invention encompasses a method of removing at least some of
16 a material from a semiconductor substrate. A feed gas is fed through
17 an ozone generator to generate ozone. The feed gas comprises at least
18 99.999% O_2 (by volume). The ozone, or a fragment of the ozone, is
19 contacted with a material on a semiconductor substrate to remove at
20 least some of the material from the semiconductor substrate.

21 In another aspect, the invention encompasses another method of
22 removing at least some of a material from a semiconductor substrate.
23 A mixture of ozone and organic solvent vapors is formed in a reaction

1 chamber. At least some of the ozone and solvent vapors are contacted
2 with a material on a semiconductor substrate to remove at least some
3 of the material from the semiconductor substrate.
4

5 **BRIEF DESCRIPTION OF THE DRAWINGS**

6 Preferred embodiments of the invention are described below with
7 reference to the following accompanying drawings.

8 Fig. 1 is a diagrammatic, cross-sectional view of a reaction chamber
9 utilized in accordance with a method of the present invention.

10 Fig. 2 is a diagrammatic, cross-sectional, fragmentary view of a
11 semiconductor wafer fragment at a preliminary processing step of a
12 method of the present invention.

13 Fig. 3 is a view of the Fig. 2 wafer fragment shown at a
14 processing step subsequent to that of Fig. 2.
15

16 **DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS**

17 This disclosure of the invention is submitted in furtherance of the
18 constitutional purposes of the U.S. Patent Laws "to promote the progress
19 of science and useful arts" (Article 1, Section 8).

20 Methodology encompassed by the present invention is described
21 with reference to Figs. 1-3. Referring initially to Fig. 1, an
22 apparatus 10 is diagrammatically illustrated. Apparatus 10 comprises a
23

1 reaction chamber 12 having a semiconductor wafer support 14 therein.
2 A semiconductor wafer 16 is shown on support 14.

3 An ozone generator 18 is shown mounted relative to chamber 12
4 such that ozone 20 formed within generator 18 is expelled into
5 chamber 12. An exemplary ozone generator is an ASTEX™ 8200, which
6 is manufactured by Applied Science and Technology, of 3500 Cabot Rd,
7 Woburn, Massachusetts. It is to be understood that ozone generator 18
8 can be mounted outside of chamber 12, and ozone flowed from generator
9 18 into chamber 12. It is also to be understood that ozone generator
10 18 could be mounted such that it is fully enclosed within chamber 12.
11 Further, it is to be understood that ozone generator 18 can be mounted
12 above wafer 16, as shown, or can be mounted in other orientations
13 relative to wafer 16.

14 A feed gas source 22 is provided externally of chamber 12, and
15 a feed gas 24 is flowed from source 22 to ozone generator 18. Feed
16 gas 24 comprises O₂, and in contrast to the prior art preferably
17 comprises at least 99.999% O₂ (by volume). Feed gas 24 is flowed into
18 ozone generator 18 to form ozone 20. An advantage of utilizing a feed
19 gas with a higher purity of oxygen than the prior art is that such
20 reduces a concentration of nitrogen within the feed gas. In accordance
21 with one aspect of the invention, it is recognized that nitrogen can be
22 converted to various nitrous oxides (NO_x) upon being passed with oxygen
23 through an ozone generator. The nitrous oxides can be corrosive and

1 otherwise damaging to integrated circuitry exposed to the nitrous oxides.
2 Further, the nitrous oxides can form various acids (such as, for example,
3 HNO_3) which can be corrosive to various integrated circuitry materials,
4 such as, for example, aluminum oxide (Al_2O_3). Accordingly, one aspect
5 of the invention encompasses utilization of a higher purity oxygen in an
6 ozone-generating feed gas than that which is utilized in the prior art.
7 A related aspect of the invention is that such utilizes an ozone-
8 generating feed gas having less nitrogen than prior art feed gases.
9 Preferably, the ozone-generating feed gas 24 comprises less than or equal
10 to 0.001% N_2 (by volume).

11 Semiconductor substrate 16 comprises an upper layer 17.
12 Semiconductor substrate 16 can comprise, for example, monocrystalline
13 silicon lightly-doped with a background p-type dopant. To aid in
14 interpretation of the claims that follow, the terms "semiconductive
15 substrate" and "semiconductor substrate" are defined to mean any
16 construction comprising semiconductive material, including, but not limited
17 to, bulk semiconductive materials such as a semiconductive wafer (either
18 alone or in assemblies comprising other materials thereon), and
19 semiconductive material layers (either alone or in assemblies comprising
20 other materials). The term "substrate" refers to any supporting
21 structure, including, but not limited to, the semiconductive substrates
22 described above. Upper layer 17 can comprise, for example, aluminum
23

1 oxide (Al_2O_3), platinum, or other materials associated with fabrication of
2 integrated circuitry.

3 A layer 19 is over upper layer 17 of semiconductor substrate 16,
4 and comprises a material which is to be removed. Layer 19 can
5 comprise, for example, photoresist, such as, for example, a so-called I-
6 line photoresist (typically a novolac resin), or a deep ultraviolet resist.
7 Alternatively, layer 19 can comprise other organic materials.

8 Ozone 20 is utilized to remove at least some of layer 19 from
9 over semiconductor substrate 16. In other words, the ozone is utilized
10 to remove a material defined by layer 19 from over the upper layer 17
11 of semiconductor substrate 16.

12 In one aspect, ozone 20 flows to material 19 to react with the
13 material and form a product which can be removed from over
14 semiconductor substrate 16. For instance, ozone 20 can oxidize an
15 organic material 19 to form a relatively volatile material which can be
16 swept from over layer 17 by flow of gases through reaction chamber 12.

17 In another aspect, ozone 20 can be broken into reactive fragments
18 which contact material 19 and react with the material to form a product
19 which can be removed from over layer 17. In the shown embodiment,
20 an ultraviolet light source 30 is provided proximate reaction chamber 12
21 and adjacent a window 32 which extends through a wall of reaction
22 chamber 12. Ultraviolet light generated by source 30 passes through
23 window 32 into chamber 12. The ultraviolet light can then impact

1 ozone 20 within chamber 12 to cause the ozone to break into reactive
2 fragments. Such reactive fragments can comprise, for example, atomic
3 oxygen. The fragments formed from the ozone can also comprise O₂.
4 In embodiments in which ozone 20 is exposed to ultraviolet light prior
5 to contact of the ozone or fragments thereof with material 19, such
6 exposure preferably occurs proximate layer 19. In such context, the term
7 "proximate" means that the exposure occurs within one foot of layer 19.
8 Such can alleviate losses of the reactive species formed by the exposure
9 prior to interaction of the reactive species with layer 19. In particular
10 aspects of the invention, the ultraviolet light can be shined onto a
11 surface of layer 19 while the surface is exposed to ozone.

12 The apparatus 10 of Fig. 1 further comprises a reservoir 50
13 comprising a volatile material 52. Reservoir 50 is on a reservoir
14 holder 54 which can comprise a heater. In operation, material 52 is
15 volatilized from reservoir 50 to form vapor within reaction chamber 12
16 which can enhance removal of material 19 by ozone 20. Volatile
17 material 52 can comprise, for example, water, and accordingly the vapor
18 formed within the reaction chamber 12 will be water vapor.
19 Alternatively, volatile material 52 could comprise an organic solvent such
20 as, for example, one or more of cyclohexanone, acetone, or propylene
21 glycol methylether acetate (PGMEA). In particular embodiments, the
22 solvent can consist essentially of, or consist of, acetone. In other
23 embodiments, the solvent can consist essentially of, or consist of,

1 cyclohexanone. In yet other embodiments, the solvent can consist
2 essentially of, or consist of, a mixture of cyclohexanone and PGMEA.
3 A particular solvent can comprise a mixture of 60% cyclohexanone and
4 40% PGMEA. An alternative solvent is propylene glycol. Although the
5 solvents described above would be liquid materials, it is to be understood
6 that reservoir 50 could also comprise a volatile solid material.

7 If the material 52 is volatile at a temperature within reactor 12,
8 vapors will be formed from material 52 without additional heating of the
9 material. Alternatively, if material 52 is not volatile at the temperature
10 of reaction chamber 12, or if it desired to enhance volatilization of
11 material 52, the material can be heated by, for example, a heater within
12 support 54.

13 If material 52 comprises a volatile organic material, then the
14 vapors formed from material 52 will be volatile organic solvent vapors.
15 It is to be understood that within the context of this document the term
16 "solvent vapor" refers to a vapor formed from a volatile organic
17 material, and not to any volatile organic materials formed by degradation
18 of layer 19 within chamber 12. If volatile solvent vapors are utilized in
19 conjunction with the very pure oxygen described above, it is preferred
20 that flames and sparks be kept out of the reaction chamber to alleviate
21 a risk of fire or explosion.

22 Although reservoir 50 is shown provided within chamber 12, it is
23 to be understood that the invention encompasses other embodiments

1 wherein reservoir 50 is provided outside of chamber 12, and wherein
2 solvent vapors are flowed into chamber 12 from the external reservoir.
3 Also, the invention encompasses embodiments wherein vapors are
4 provided in a gas source external of chamber 12 (such as, for example,
5 a tank of gas), and piped into chamber 12.

6 Organic solvent vapors are found to assist in removal of organic
7 materials 19 (such as, for example, photoresist) from over semiconductor
8 substrates. A possible mechanism is that the vapors may "wet" or
9 otherwise improve susceptibility of an organic material 19 to ozone or
10 reactive fragments formed from ozone. Such mechanism is provided to
11 assist in understanding the present invention, and is not to limit the
12 claims except to the extent that the mechanism is expressly recited within
13 a claim.

14 Figs. 2 and 3 illustrate enlarged views of the semiconductor
15 substrate 16 at processing steps of a method of the present invention.
16 Fig. 2 illustrates semiconductor substrate 16 having material 19 thereover.
17 Specifically, material 19 is over a layer 17. As discussed above, layer 19
18 can comprise an organic material such as, for example, photoresist.
19 Layer 17 can comprise an inorganic material such as, for example,
20 aluminum oxide or platinum.

21 Referring to Fig. 3, semiconductor substrate 16 is illustrated after
22 material 19 has been removed from over layer 17. Such removal can be
23 accomplished by the processing described above with reference to Fig. 1,

1 wherein ozone (or a reactive fragment generated from ozone) is
2 contacted with material 19 to remove material 19. It is noted that some
3 of layer 17 can be exposed to the ozone, or ozone fragments, during
4 removal of material 19. In accordance with an embodiment of the
5 present invention, the ozone preferably will be formed from an oxygen
6 feed material that comprised less than 0.001% nitrogen. Accordingly,
7 any concentration of nitrous oxides or reactive products formed from
8 nitrous oxides will be lower in methods of the present invention than in
9 prior art processes. Accordingly, if layer 17 comprises aluminum oxide,
10 platinum, or other materials which can be etched or otherwise corroded
11 by nitrous oxide or products thereof, methods of the present invention
12 can alleviate such corrosion relative to prior art methods.

13 In compliance with the statute, the invention has been described
14 in language more or less specific as to structural and methodical
15 features. It is to be understood, however, that the invention is not
16 limited to the specific features shown and described, since the means
17 herein disclosed comprise preferred forms of putting the invention into
18 effect. The invention is, therefore, claimed in any of its forms or
19 modifications within the proper scope of the appended claims
20 appropriately interpreted in accordance with the doctrine of equivalents.
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